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Occurrence of Guaiacyl Lignin in Angiospermous Species, *Sarcandra glaber* and *Sarcandra spicatus*.

Toru SHIO* and Takayoshi HIGUCHI**

Abstract—Lignins of two vesselless angiospermous species, *Sarcandra glaber* and *Sarcandra spicatus*, gave mainly vanillin, 4-ethoxy-3-methoxybenzoic acid, and guaiacylpropanones in alkaline nitrobenzene oxidation, permanganate oxidation after ethylation, and acidolysis, respectively and low methoxyl contents as in coniferous lignin. IR spectra of the lignins also showed characteristics of coniferous lignin. These data indicated that both plants contain guaiacyl lignin as has been suggested by Mäule negative reactions.

Introduction

It has been established that guaiacyl lignin generally occurs in gymnosperms but not in angiosperms except some limited species such as *Erythrina crista-galli* which is found to contain guaiacyl lignin¹⁾. Since the xylem tissue of *Sarcandra glaber* was found to give a negative Mäule test²⁾ (brown color) as in coniferous lignin, the occurrence of guaiacyl lignin in this species is suggested although no characterization of the *Sarcandra* lignin has been carried out. Here, evidence for the occurrence of guaiacyl lignin in the both species is reported as a part of the studies on the relation between lignin and plant phylogeny.

Plant material—Stems of *Sarcandra glaber* and *Sarcandra spicatus* which grew in the green house of the Wood Research Institute, Kyoto University were collected in July, 1979. The stems were cut into small pieces which were air-dried and then pulverized using a small Wiley mill. The powder was extracted with ethanol-benzene (1:2) by a Soxhlet's extractor for 48 hr and with hot water for 40 hr, successively before use.

Methoxyl contents and IR spectra—Lignins of the both plants were prepared by a Klason method and methoxyl contents were determined by a modified Zeisel method. IR spectra of the lignins were taken as KBr tablet by a Jasco model IR-S, and the relative absorptivities ($A/A_{1505\text{ cm}^{-1}}$) of characteristic maxima were calculated.³⁾

Alkaline nitrobenzene oxidation—Stem powder (200 mg), 8% NaOH (10 ml) and nitrobenzene (0.2 ml) were added in a small stainless steel autoclave which were kept

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in an oil bath at 170°C for 2 hr with occasional shaking. The contents were filtered after cooling to room temperature and the filtrate was extracted with ether to remove excess nitrobenzene. The aqueous solution was then acidified to pH 2 and extracted 4 times with ether using a separating funnel. The combined ether extract was concentrated *in vacuo*, and the residue was dissolved in a definite amount of ethanol for GC-MS analysis by Shimadzu-LKB 9000 mass-spectrometer.³⁾ Column; DC 200, 5% (2 m), 185°C. The compounds were identified by the retention time and the mass spectra in comparison with those of authentic compounds.

Permanganate oxidation of ethylated wood powder—Wood powder was ethylated with diethyl sulfate and 10 N NaOH and the ethylated wood powder were subjected to permanganate oxidation as reported previously³⁾. The aromatic acids thus obtained were methylated to their methyl ester with diazomethane and analyzed by GC-MS. Column; OV-1, 1% (2 m), 180°C.

Acidolysis—Wood powder (200 mg) was suspended in 10 ml of a mixture of dioxane-water (9:1) containing 0.1 N hydrogen chloride and refluxed for 4 hr. The reaction mixture was filtered and the filtrate was added dropwise into 150 ml of water with stirring. The precipitated dioxane lignin was filtered and the filtrate was extracted with CHCl_3 . The CHCl_3 extract was concentrated *in vacuo*. The acidolysis monomers were converted to TMS derivatives and analyzed by GC-MS³⁾. Column; OV-1, 1% (2 m), 190°C.

Results and Discussion

Analytical results of *Sarcandra* lignins are given in Table 1. Both lignins gave negative Mäule reactions and their methoxyl contents were close to that of coniferous lignin: it is known that methoxyl contents of angiosperm lignins are about 20% and that of coniferous lignin is about 15%, respectively on the average. The IR spectra of both lignins also gave characteristics of coniferous lignin: the relative absorptivities ($A/A_{1505\text{ cm}^{-1}}$) of characteristic maxima⁴⁾ and that of ($A_{1275\text{ cm}^{-1}}/A_{1235\text{ cm}^{-1}}$)¹⁾ showed that the lignins are guaiacyl lignin.

Table 1. Methoxyl contents and Mäule reaction of *Sarcandra* lignin

	OCH ₃ (%)	Mäule reaction
<i>Sarcandra glaber</i>	13.8	—
<i>Sarcandra spicalus</i>	13.4	—

Gas chromatogram of the products in nitrobenzene oxidation of *Sarcandra glaber* lignin is shown in Fig. 1. The products of the lignin mainly contain vanillin (1) with a trace amount of syringaldehyde (2) indicating that the lignin is a guaiacyl lignin.

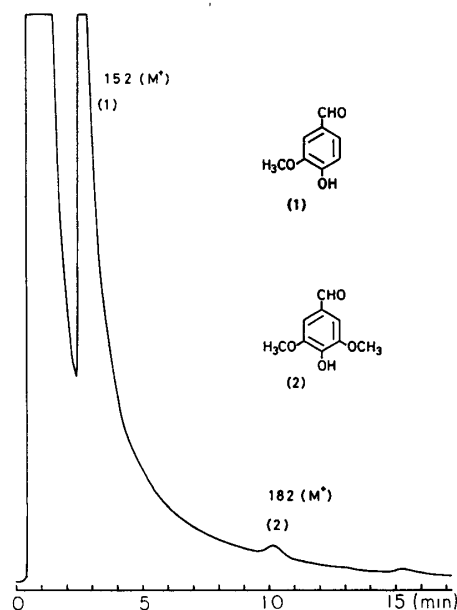


Fig. 1. Gas chromatogram of the aromatic aldehydes obtained by alkaline nitrobenzene oxidation of wood (*Sarcandra glaber*). Column: DC 200, 5% (2m), 185°C

A very similar pattern of the chromatogram was found for the lignin of *Sarcandra spicatus*.

Fig. 2 shows the chromatogram of permanganate oxidation products of the ethylated lignin of *Sarcandra glaber*. A major peak of 4-ethoxy-3-methoxybenzoic acid

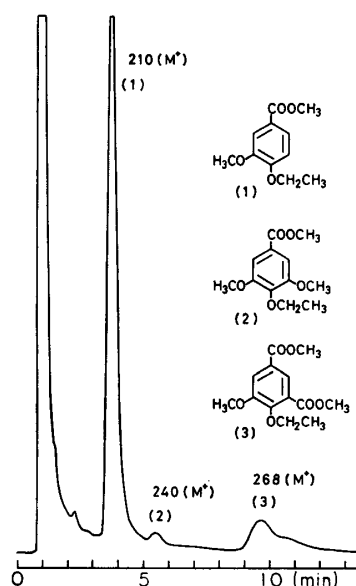


Fig. 2. Gas chromatogram of the aromatic acids obtained by permanganate oxidation of ethylated wood (*S. glaber*). Column: OV-1, 1% (2m), 180°C

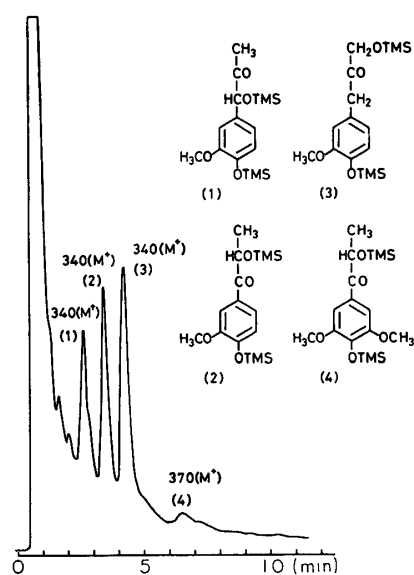


Fig. 3. Gas chromatogram of the acidolysis monomers of wood (*S. glaber*). Column: OV-1, 1% (2m), 190°C

methyl ester (1) was found with a small amount of 4-ethoxy-3-methoxyisophthalic acid dimethyl ester (3) and a trace amount of 4-ethoxy-3,5-dimethoxybenzoic acid methyl ester (2). The chromatogram of permanganate oxidation products of *Sarcandra spicatus* lignin was very similar to that of *Sarcandra glaber*. These results are in harmony with the results in nitrobenzene oxidation of the lignins.

The gas chromatogram of the acidolysis products of the lignin of *Sarcandra glaber* is shown in Fig. 3. 1-Hydroxy-(3-methoxy-4-hydroxyphenyl)-2-propanone (1), 2-hydroxy-1-(3-methoxy-4-hydroxyphenyl)-1-propanone (2), β -oxyconiferyl alcohol (3) and small amounts of the corresponding syringylpropanones (4) were identified by GC-MS in the acidolysis monomers. A similar result was obtained for the acidolysis products of *Sarcandra spicatus*. The result confirmed that the lignins are guaiacyl lignin.

It has been found that the lignin in the primary xylem of a young poplar⁵⁾ and the lignin of leaf-stalks^{6,7)} of various higher plants which contain no secondary xylem is mainly composed of guaiacyl component with very small amounts of syringyl one: lignin in secondary xylem contains increasing amounts of syringyl component. *Sarcandra* plants are vasselles small shrubs, and the stem of which is only 3–6 mm in diameter with a very small amount of secondary xylem because of the poor secondary thickenings. Such anatomical characteristics of the stem in these relatively primitive angiosperms may be related to the formation of guaiacyl lignin.

Acknowledgment

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